

XII. *On the Action of the Rays of the Solar Spectrum on Vegetable Colours, and on some new Photographic Processes.* By Sir JOHN F. W. HERSCHEL, Bart. K.H. F.R.S.

Received June 15,—Read June 16, 1842.

149\*. IN my paper on the “Chemical Action of the Solar Spectrum on preparations of Silver and other substances,” read to the Royal Society in February 1840, and of which the present communication is intended as a continuation or supplement, some experiments on the effect of the spectrum on the colouring matter of the *Viola tricolor*, and on the resin of guaiacum are described, which the extreme deficiency of sunshine during the summer and autumn of the year 1839 prevented me from prosecuting efficiently up to the date of that communication. The ensuing year 1840 was quite as remarkable for an excess of sunshine as its predecessor for the reverse. Unfortunately the derangements consequent on a change of residence prevented my availing myself of that most favourable conjuncture, and it was not till the autumn of that year that the inquiry could be resumed. From that time to the present date it has been prosecuted at intervals as the weather would allow, though owing to the almost unprecedented continuance of bad weather during the whole of the past summer and autumn (1841), it has of late been almost wholly suspended†. In photographic processes, where silver and other metals are used, the effect of light is so rapid that the state of the weather, as to gloom or sunshine, is of little moment. It is otherwise in the class of photographic actions now to be considered, in which exposure to the concentrated spectrum for many hours, to clear sunshine for several days, or to dispersed light for whole months, is requisite to bring on many of the effects described, and those some of the most curious. Moreover, in such experiments, when unduly prolonged by bad weather, the effects due to the action of light become mixed and confounded with those of spontaneous changes in the organic substances employed, arising from the influence of air, and especially of moisture, &c., and so give rise to contradictory conclusions, or at all events preclude definite results, and obscure the perception of characters which might serve as guides in an intricate inquiry, and afford hints for the conduct of future experiment. It is owing to these causes that I am unable to present the results at which I have arrived, in any sort of regular or systematic connection; nor should I have ventured to present them at all to the Royal Society, but in the hope that, desultory as they are, there may yet be

\* The paragraphs, for convenience of reference, are numbered in continuation of those of the previous paper referred to in the text.

† This was written in April 1842, since which a repetition of the season of 1840 seems to have commenced.

found in them matter of sufficient interest to render their longer suppression unadvisable, and to induce others more favourably situated as to climate, to prosecute the subject.

150. The materials operated on in these experiments have been for the most part the juices of the flowers or leaves of plants, expressed, either simply, or with addition of alcohol, or under the influence of other chemical reagents. Some few resinous and dyeing substances have also been subjected to experiment, but with less perseverance than the obvious practical importance of this branch of the subject might demand, except in the case of *guaiacum*, whose relations to light, heat, and chemical agents are exceedingly remarkable and instructive, for which reason, as well as because some of these relations have been treated of in my former paper, I shall commence the account of my later experiments with those made on this substance. But in the first place it is necessary to state that the apparatus used for forming, concentrating, and fixing the spectrum, was the same with that described in Art. 67. of that paper; the prism being that of flint-glass by *FRAUNHOFER*, there mentioned; the area of the section of the incident sunbeam = 1.54 square inch, and the dimensions of the principal elements of the luminous spectrum, identical with those recorded in §. 70, so that the following results, when numerically stated (in measures of which the unit is one-thirtieth of an inch), will be comparable with those previously described. To spare reference, however, it may be here mentioned that the diameter of the sun's image in the focus of the achromatic lens used is 7.20 of such thirtieths; and that the extent of the visible spectrum corrected for the sun's semidiameter at either end, equals 53.92 thirtieths, of which 13.30 are considered as reckoned negatively to the extreme visible red from a fiducial point or centre corresponding to the mean yellow ray; and 40.62 positively, from the same centre to the terminal violet, both as seen through a certain standard blue glass, which lets both extremes pass freely and insulates the mean yellow with considerable precision. The correction for the sun's semidiameter has been applied in what follows to all measures up to *terminations of spectra*, unless where the contrary is expressed. Maxima and minima of action, and neutral points neither require nor admit this correction.

#### *Guaiacum.*

151. A solution of this resin in alcohol, spread evenly on paper, gives a nearly colourless ground. A slip of this paper exposed to the spectrum is speedily impressed with a fine blue streak over the region of the violet rays, and far beyond, as described in Art. 92. If the paper during this action be carefully defended from extraneous light, this is the only perceptible effect; but if dispersed light be admitted, the general ground of the paper is turned to a pale brownish green, with exception of that portion on which the less refrangible rays fall, which, by their agency, is defended from the action of the dispersed light and preserves its whiteness, as in the case of the argentine paper described in Art. 60. The spectrum, therefore, ultimately impressed,

Fig. 1. Art. 151.



Fig. 2. Art. 153.



Fig. 3. Art. 155.



Fig. 4. Art. 176.

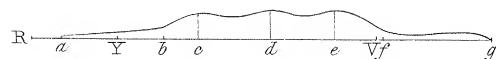


Fig. 5. Art. 176.



Fig. 6. Art. 188.



Fig. 7. Art. 191.

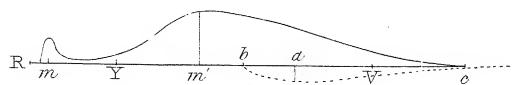
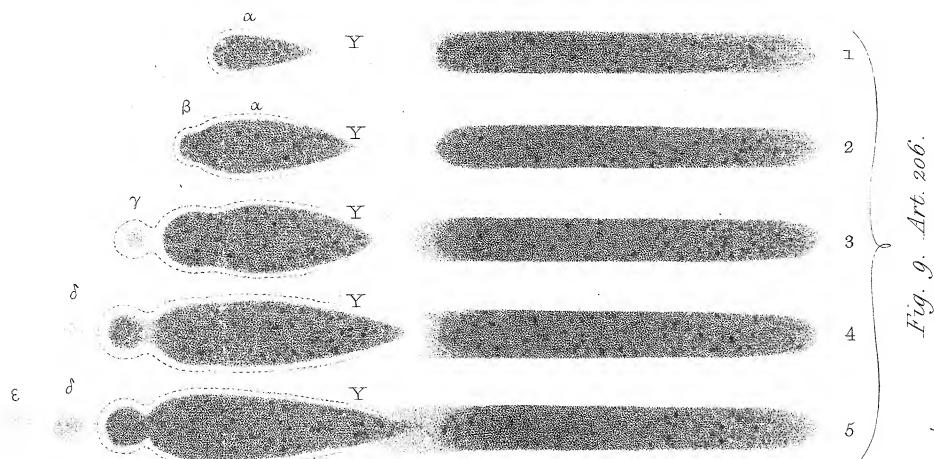
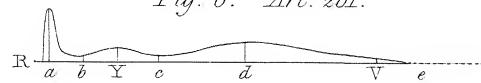


Fig. 8. Art. 201.



Thermographic Impressions.

Photographic Impressions.

Fig. 12. Art. 244.

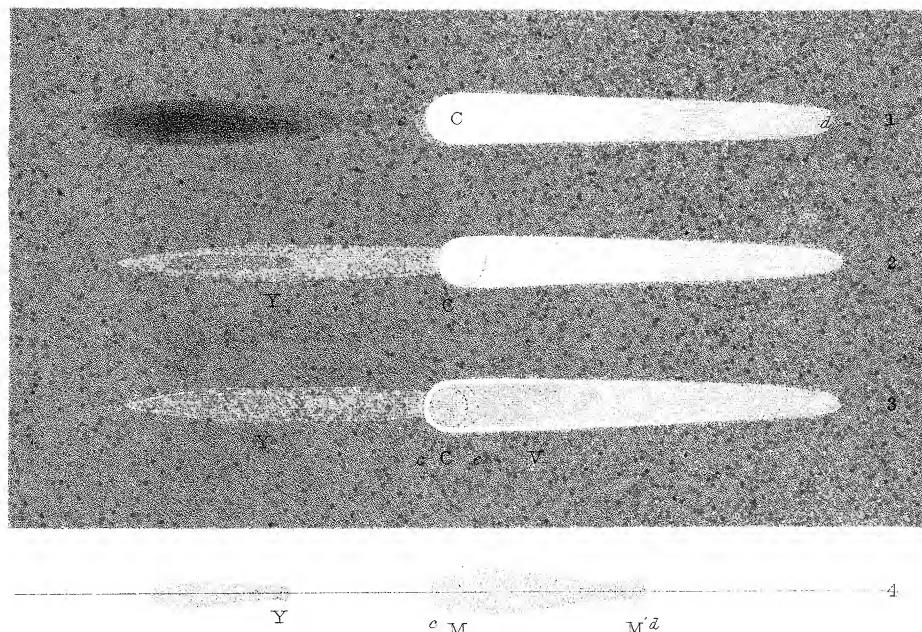


Fig. 10. Art. 207.

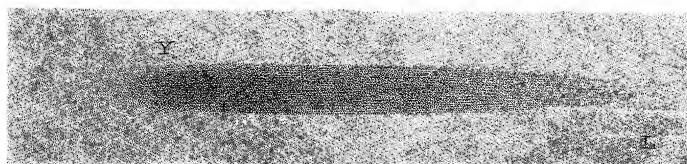
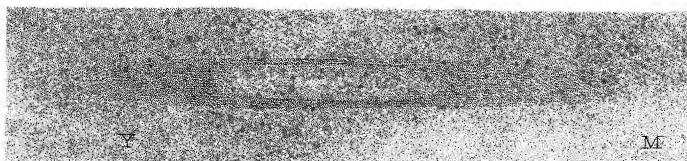


Fig. 11. Art. 212.



consists of two portions similar to those described in Art. 93, and of nearly the same extent, that is to say, a white or pale yellowish portion having its maximum of intensity at  $0\cdot 0$ , and extending from  $-11\cdot 9$  (corrected for the sun's semidiameter) to  $+12\cdot 0$ , or thereabouts, at which point the character of the action changes, and a blue, of a somewhat smoky grey cast, commences, which attains a maximum at  $+40\cdot 0$ , thence degrades to an intermediate minimum at  $+47\cdot 0$ , attains a second and much stronger maximum at  $+61\cdot 0$ , and ceases at  $72\cdot 4$ . The precise numbers vary materially in different specimens and with the length of exposure. The type of this spectrum, of its natural length, is represented in Plate XV. fig. 1, in which the abscissæ being measured along the length of the spectrum, from the fiducial centre Y both ways, the ordinates express the intensities of photographic action at each corresponding point, as estimated from the amount of colour induced or prevented. In this type the portion corresponding to the less refrangible rays is represented by negative values of the ordinate agreeably to Art. 93, where it is shown that these rays not only prevent the blue colour from being produced by the more refrangible ones, but destroy it when so produced. Another specimen gave the following dimensions:  $Y a = -11\cdot 4$ ,  $Y b = -9\cdot 5$ ,  $Y c = +30\cdot 0$ ,  $Y d = +61\cdot 0$ ,  $Y e = +80\cdot 4$ , and this is the greatest extent of action I have hitherto observed.

152. A portion of the same paper was exposed, dry, to an atmosphere of chlorine considerably diluted with common air, which imparted to it a pale, dirty, greenish yellow hue. Being thence transferred immediately to the spectrum, the result was not a little remarkable. The whole spectrum, the green excepted, was impressed in faint tints nearly corresponding to the natural ones. The red was evident—the yellow dilute and nearly white—the blue a fine sky-blue, while beyond the violet succeeded a train of somewhat greenish darkness. These tints proved fugitive, and in twenty-four hours were nearly obliterated.

153. When paper fresh washed with tincture of guaiacum and still wet is exposed to chlorine, it instantly acquires a fine and full Prussian blue colour, which however passes speedily to brown if the action be prolonged. The colour is difficult to preserve in its full intensity, and fades considerably in drying, becoming at the same time somewhat greenish. Exposed wet to the spectrum, it is found to have become much more sensitive, and is immediately attacked with great energy by the red rays, which destroy the blue colour, converting it to a brownish or reddish yellow. The action extends rapidly up the spectrum as far as the extreme violet, in which ray, however, the tint impressed or left undestroyed passes to a hue partaking of violet, and indicating by the change what ought probably to be regarded as a neutral point at  $+12\cdot 0$ . The impressed spectrum (corrected for semidiameter) commences at  $a$ , fig. 2, at  $-13\cdot 4$ ; the maximum  $b$  of the positive action occurs at  $-9\cdot 0$ , the neutral point  $c$  at  $+12\cdot 0$ , the maximum  $d$  of negative action at  $+33\cdot 0$ , and the sensible termination  $e$  of the impression at  $+60\cdot 0$ .

154. The action of gaseous chlorine is too energetic to be easily arrested at the

proper point, besides which this gas also acts powerfully on the alcohol employed. To obviate these inconveniences, paper thoroughly impregnated with guaiacum by washing with the tincture, and drying in a gentle heat, was steeped in weak aqueous solution of chlorine, by which process it slowly acquired a beautiful and pure celestial blue colour. It is very sensitive, and may be conveniently used for copying engravings, &c., which it does with this singularity, that the picture penetrates the paper and appears on the back of very nearly the same intensity as on the face\*. Indeed, if the picture be over sunned the back will exhibit a perfect impression, while the face is spoiled, which produces a very strange effect: exposed to the spectrum, the blue colour is converted to a pale reddish yellow in the region of the less refrangible rays, and simply whitened in the more refrangible region. The action, when prolonged till the light seems to have no further influence, extends from  $-12\cdot4$ , corrected for semidiameter, to  $+40$ , or thereabouts, where it dies away insensibly. The maximum of photographic action occurs at  $-8\cdot7$ , and some trace of a minimum is perceptible at  $+11\cdot5$ . Photographs taken on this paper, or spectra impressed on it, are fugitive—lose much of their force and beauty in a few days, and at length vanish altogether.

155. When paper is washed with a solution of guaiacum in soda it acquires a green colour, though the solution itself is brown. By inclining the paper and carrying the wash always from below upwards, a very even tint may be obtained. The excess of liquid being blotted off, aqueous solution of chlorine was poured over it (on a slope) till all the alkali was saturated, and the liquid ran off smelling strongly of chlorine. Thus was produced a paper (No. 1168.) very evenly tinted, and varying in colour from a deep, somewhat greenish, to a fine celestial blue, according to the strength of the solutions employed. It is very sensitive, and is attacked with especial energy by rays in the spectrum, ranging from  $-11\cdot4$  to  $+11\cdot4$  with a maximum at  $-9\cdot0$ , the type being as in fig. 3.

156. When paper so prepared is exposed, wet, to a temperature of  $212^{\circ}$  FAHR., it is immediately discoloured, the green changing to a sere or brownish yellow. The same change is produced after some little time at a temperature of  $190^{\circ}$ , and still more slowly, though yet completely, at  $180^{\circ}$ . At  $175^{\circ}$  the discolouration is incomplete and very slow; and below that temperature the colour is not affected. If the paper be perfectly dried in a temperature gradually raised to  $212^{\circ}$ , the discolouration requires a considerably higher temperature, ranging from  $220^{\circ}$  to  $275^{\circ}$ , according to the time of exposure, being very slow at the former limit and almost immediate at the latter. These changes are independent of the action of light, being produced under mercury.

157. The destruction by heat of the green or blue colour superinduced on guaiacum by the more refrangible rays of light, was noticed by WOLLASTON, and it would seem, on a consideration of his experiments and of those described in the last article, that nothing further is requisite for operating the change from the green or blue to

\* For another remarkable case of this kind see the Postscript to this paper.

the yellow state, than the assumption of a certain temperature dependent on its state of dryness, and varying according to that state between the limits of  $180^{\circ}$  and  $280^{\circ}$ . Nevertheless, if we consider that the same change is produced by rays of the spectrum which are very far from being the *hottest*, while yet the extra-spectral thermic rays, under precisely the same circumstances of exposure, produce no such effect, though far surpassing in mere calorific power those which do, we shall see reason to doubt the sufficiency of this view of the matter. The following experiments were therefore instituted with a view to its further elucidation.

158. A slip of the paper No. 1168 was moistened and subjected in clear sunshine to the action of the spectrum. The colour was discharged from the region occupied by the less refrangible luminous rays, as described in Art. 155. At the same time, the more distant thermic rays beyond the spectrum produced their proper effect, in evaporating the moisture from those portions on which they fell; so that in due time the *heat-spots*  $\delta$  and  $\gamma$  became apparent (see Art. 136), the former very distinctly, the latter perceptibly. The spot  $\beta$  (which is remarkable) was scarcely if at all formed. So long then as the paper continued moist and remained under the influence of the thermic rays, the appearances were those of *a diminution of colour* (Art. 131.), operated by the thermic rays  $\delta$  and  $\gamma$ . But the discolouration in these points was only apparent, for as the paper dried these *heat-spots* disappeared, leaving its colour quite unchanged at those points; while the photographic impression really produced within the visible spectrum, remained and went on increasing in intensity. The non-luminous thermic rays, therefore, though clearly shown to have been active *as heat*, were yet incapable of effecting that peculiar chemical change which other rays much less copiously endowed with heating power, were all the while producing.

159. It may be objected to this, that no proof is afforded in the above-related experiment, that any part of the paper actually attained a temperature of  $180^{\circ}$  or more; that in consequence no discolouration due to the action of heat (*quoad heat*) was produced; and that the discolouration which did take place was *sui generis*, and originated with the *light and not the heat* of that part of the spectrum to which it corresponded. A slip of the same paper (1168.) was therefore exposed dry to the spectrum in such a way as to leave its back accessible; and an iron heated below redness was then approached to it so as *just not* to discolour the paper. Under such circumstances it might be expected that the additional heat thrown on the paper in the region of the thermic rays would turn the scale in their favour at their points of greatest intensity, and give ocular proof of their action by a decided discharge of colour at those points. But no such result was obtained, nor could I succeed in rendering visible any of the heat-spots  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , even when the heated iron was brought so near as to produce a commencement of discolouration over the whole of that region of the paper where they ought to have shown themselves.

160. On the other hand, a remarkable, but by no means an unexpected, influence was exercised by the heat so thrown on that part of the paper where the less refran-

gible rays fell, and where the discolouration was in progress under their agency. For it was observed that, under these circumstances, the discolouration in question went on with much greater rapidity, so much so indeed, that the same amount of it, which without extraneous heat would have required twenty minutes or half an hour's exposure to the spectrum to produce, was now produced in two or three minutes. Obscure terrestrial heat, therefore, is shown to be capable of *assisting* and *being assisted* in operating this peculiar change, by those rays of the spectrum, whether luminous or thermic, which occupy its red, yellow, and green regions; while on the other hand it receives no such assistance from the purely thermic rays beyond the spectrum, acting under precisely similar circumstances, and in an equal state of condensation.

161. When heat was similarly applied by radiation from behind, and from a non-luminous source, over the *more* refrangible region of a spectrum thrown on paper simply washed with tincture of guaiacum and not previously blued either by chlorine or by light, the blue colour induced in the *more* refrangible rays was still produced, and of the same tint in the same points as if no heat had acted. This effect, the contrary to what the previous experiment would have led to expect, shows how little any reasonings on these points enable us at present to anticipate experience.

162. The discharge of colour from blued guaiacum by mere heat, has been shown above (Art. 156.) to take place at a much lower temperature in the presence of moisture than when dry; and a similar destruction of colour, under similar circumstances, takes place with many other vegetable preparations. Paper, for instance, coloured with the juice of the *Viola tricolor* (Art. 90.), is speedily whitened in the dark, while wet, by the heat of boiling water, though dry heat does not affect it. And under the action of the spectrum it is discoloured (though much more slowly) by the same, or nearly the same rays which are effective in the case of guaiacum. The colour of paper tinged with the juice of the common red stock is not affected when dry by any heat short of what suffices to scorch the paper, but when wet (as when exposed to steam) it is speedily discharged. There are few, if any vegetable colours indeed which long resist the combined effects of heat and moisture, even when light is excluded, still less when admitted\*.

*Of the Colours of Flowers in general under the action of the Spectrum.*

163. In operating on the colours of flowers I have usually proceeded as follows:—the petals of the fresh flowers, or rather such parts of them as possessed a uniform tint, were crushed to a pulp in a marble mortar, either alone, or with addition of alcohol, and the juice expressed by squeezing the pulp in a clean linen or cotton cloth. It was then spread on paper with a flat brush, and dried in the air without artificial

\* On the effects of light, air, and moisture at common temperatures, as discolouring agents on several dyeing materials, I may refer to M. CHEVREUL's elaborate memoir (Acad. R. des Sciences, tom. xvi.). M. CHEVREUL's experiments, however, relate to the action of light simply as it comes from the sun without prismatic separation, and have therefore little or nothing in common with the objects of this paper.

heat, or at most with the gentle warmth which rises in the ascending current of air from an Arnott stove. If alcohol be not added, the application on paper must be performed immediately, since exposure to the air of the juices of most flowers (in some cases even for but a few minutes) irrecoverably changes or destroys their colour. If alcohol be present this change does not usually take place, or is much retarded; for which reason, as well as on account of certain facilities afforded by its admixture in procuring an even tint (to be presently stated), this addition was commonly, but not always made.

164. Most flowers give out their colouring matter readily enough, either to alcohol or water. Some, however, as the *Escholzias* and *Calceolarias*, refuse to do so, and require the addition of alkalies, others of acids, &c. When alcohol is added, it should, however, be observed that the tint is often, apparently, much enfeebled, or even discharged altogether, and that the tincture, when spread on paper, does not reappear of its due intensity till after complete drying. The temporary destruction of the colour of the blue heartsease by alcohol has been noticed in my former paper (Art. 90.), nor is that by any means a singular instance. In some, but in very few cases, it is destroyed, so as neither to reappear on drying, nor to be capable of revival by any means tried. And in all cases long keeping deteriorates the colours and alters the qualities of the alcoholic tinctures themselves, so that they should always be used as fresh as possible.

165. If papers tinged with vegetable colours are intended to be preserved, they must be kept perfectly dry and in darkness. A close tin vessel, the air of which is dried by quicklime (carefully enclosed in double paper bags, well pasted at the edges to prevent the dust escaping), is useful for this purpose. Moisture (as already mentioned, especially assisted by heat) destroys them for the most part rapidly, though some (as the colour of the *Senecio splendens*) resist obstinately. Their destructibility by this agency, however, seems to bear no distinct relation to their photographic properties.

166. This is also the place to observe that the colour of a flower is by no means always, or usually, that which its expressed juice imparts to white paper. In many cases the tints so imparted have no resemblance to the original hue. Thus, to give only a few instances, the red damask rose of that intense variety of colour, commonly called by florists the Black Rose, gives a dark slate blue, as do also the clove carnation and the black holyoak; a fine dark brown variety of *Sparaxis* gave a dull olive green; and a beautiful rose-coloured tulip, a dirty bluish green; but perhaps the most striking case of this kind is that of a common sort of red poppy (*Papaver Rheum?*), whose expressed juice imparts to paper a rich and most beautiful blue colour, whose elegant properties as a photographic material will be further alluded to hereafter\*.

\* A semicultivated variety was used, having dark purple spots at the bases of the petals. The common red poppy of the chalk (*Papaver hybridum*) gives a purple colour much less sensitive and beautiful.

167. This change of colour is probably owing to different causes in different flowers. In some it undoubtedly arises from the escape of carbonic acid, but this as a general cause for the change from red to blue, has, I am aware, been controverted\*. In some (as is the case with the yellow Ranunculi) it seems to arise from a chemical alteration depending on absorption of oxygen; and in others, especially where the expressed juice coagulates on standing, to a loss of vitality or disorganization of the molecules. The fresh petal of a single flower, merely crushed by rubbing on dry paper, and instantly dried, leaves a stain much more nearly approximating to the original hue. This, for example, is the only way in which the fine blue colour of the common field Veronica can be imparted to paper. Its expressed juice, however quickly prepared, when laid on with a brush, affords only a dirty neutral gray, and so of many others. But in this way no even tint can be had, which is a first requisite to the experiments now in question, as well as to their application to photography.

168. To secure this desirable evenness of tint, the following manipulation will generally be found successful. The paper should be moistened at the back by sponging and blotting off. It should then be pinned on a board, the moist side downwards, so that two of its edges (suppose the right-hand and lower ones) shall project a little beyond those of the board. The board being then inclined twenty or thirty degrees to the horizon, the alcoholic tincture (mixed with a very little water, if the petals themselves be not very juicy) is to be applied with a brush in strokes from left to right, taking care *not to* go over the edges which rest on the board, but *to* pass clearly over those which project, and observing also to carry the tint from below upwards by quick sweeping strokes, leaving no dry spaces between them, but keeping up a continuity of wet surface. When all is wet, cross them by another set of strokes from above downwards, so managing the brush as to leave no floating liquid on the paper. It must then be dried as quickly as possible over a stove, or in a current of warm air, avoiding, however, such heat as may injure the tint. The presence of alcohol prevents the solution of the gummy principle, which, when present, gives a smeary surface; but the evenness of tint given by this process results chiefly from that singular intestine movement which always takes place when alcohol is in the act of separation from water by evaporation—a movement which disperses knots and blots in the film of liquid with great energy, and spreads them over the surrounding surface.

169. The action of the spectrum, or of white light, on the colours of flowers and leaves, is extremely various, both as regards its total intensity and the distribution of the active rays over the spectrum. But certain peculiarities in this species of action obtain almost universally.

1st. The action is *positive*, that is to say, light destroys colour; either totally, or leaving a residual tint, on which it has no further, or a very much slower action. And thus is effected a sort of chromatic analysis, in which two distinct elements of

\* NICHOLSON's Journal.

colour are separated, by destroying the one and leaving the other outstanding. The older the paper, or the tincture with which it is stained, the greater is the amount of this residual tint.

2nd. The action of the spectrum is confined, or nearly so, to the region of it occupied by the luminous rays, as contra-distinguished both from the so-called chemical rays, beyond the violet, which act with the chief energy on argentine compounds, but are here for the most part ineffective, on the one hand, and on the other, from the thermic rays beyond the red, which appear to be totally so. Indeed, I have hitherto observed no instance of the extension of this description of photographic action on vegetable colours beyond, or even *quite* up to the extreme red.

170. Besides these, it may also be observed that the rays effective in destroying a given tint, are, in a great many cases, those whose union produces a colour complementary to the tint destroyed, or at least one belonging to that class of colours to which such complementary tint may be referred. For example, yellows tending towards orange are destroyed with more energy by the blue rays; blues by the red, orange, and yellow rays; purples and pinks by yellow and green rays.

171. These are certainly remarkable and characteristic peculiarities, and must indeed be regarded as separating the luminous rays by a pretty broad line of chemical distinction from the non-luminous; though whether they act *as such*, or in virtue of some peculiar chemical quality of the heat which accompanies them *as heat*, is a point which the experiments on guaiacum, above described, seem to leave rather equivocal. In the latter alternative, chemists must henceforward recognize differences not simply of intensity, but of quality in heat from different sources; of quality, that is to say, not merely as regards degree of refrangibility or transcalescence, but as regards the strictly chemical changes it is capable of effecting in ingredients subjected to its influence.

172. As above stated, these peculiarities, at least the first two, obtain almost universally. Exceptions, however, though very rare, do occur, as will be more particularly mentioned hereafter. The third rule is much less general, and is to be interpreted with considerable latitude; but among its exceptions I have been unable to detect any common principle capable of being distinctly enunciated.

173. Lastly, it requires to be expressly mentioned, that the habitudes of the colours, both of the flowers and leaves of plants, with relation either to white light or to the prismatic rays, vary materially with the advance of the season, and perhaps also with the hour of the day at which they are gathered. Generally speaking, so far as I have been able to observe, the earlier flowers of any given species reared in the open air (provided they are well ripened, i. e. the colour fully developed) are more sensitive than those produced even from the same plant, at a late period in its flowering, and have their colours more completely discharged by light. As the end of the flowering period comes on, not only the destruction of the colour by light is slower, but residual tints are left which resist obstinately. A very remarkable case of this kind was no-

ticed in *Chryseis californica*, the earliest flowers of which exhibited in the photograph of their spectrum a well-insulated round spot, eaten away by red rays almost at its extremity, which spot I never was able to reproduce with later flowers from the same root. Those gathered at the end of its flowering also left a residual yellow of extreme obstinacy\*, which was by no means the case with the earlier flowers.

174. It would be waste of time to enumerate all the vegetable tints which I have subjected to experiment, comprising most of the ordinary hardy garden and wild flowers of the country. To the rarer and more splendid species which adorn the stoves and greenhouses of florists, I have had little access, a circumstance I much regret, and which leads me to take this opportunity of mentioning, that specimens of paper stained with the juices of highly-coloured, or otherwise remarkable flowers or leaves, either by alcoholic extraction, or by simple expression (if accompanied with the botanical name of the plant used), will be highly acceptable, from whatever quarter received. I shall here set down only those which afforded some ground for special remark, so far as I have yet pushed the inquiry.

#### *Colours of particular Flowers.*

175. *Corchorus Japonica*.—The flowers of this common and hardy but highly ornamental plant, are of a fine yellow, somewhat inclining to orange, and this is also the colour the expressed juice imparts to paper. As the flower begins to fade *the petals whiten*, an indication of their photographic sensibility, which is amply verified on exposure of the stained paper to sunshine. I have hitherto met with no vegetable colour so sensitive. If the flowers be gathered in the height of their season, paper so coloured (which is of a very even and beautiful yellow) begins to discolour in ten or twelve minutes in clear sunshine, and in half an hour is completely whitened. The colour seems to resist the first impression of the light, as if by some remains of vitality, which being overcome, the tint gives way at once, and the discolouration when commenced goes on rapidly. *It does not even cease in the dark when once begun.* Hence it happens that photographic impressions taken on such paper, which when fresh are very sharp and beautiful, fade by keeping, visibly from day to day, however carefully preserved from light. Specimens of such photographs (copies of engravings) are submitted with this paper for inspection. They require from half an hour to an hour to complete, according to the sunshine. Hydriodate of potash cautiously applied, retards considerably, but does not ultimately prevent, this spontaneous discharge.

176. Exposed to the spectrum, in about fifteen or twenty minutes the colour is totally destroyed and the paper whitened in the whole region of the green, blue and violet rays, to which therefore the most energetic action is confined, agreeably to the law of complementary tints (Art. 170.). If the action of the spectrum be prolonged,

\* Probably, therefore, useful in dyeing. The species is that most commonly cultivated in gardens, with bright yellow petals having orange-coloured bases.

a much feebler whitening becomes sensible in the red, and a trace of it also beyond the violet into the "lavender" rays. In this state the type of the impressed spectrum (in an experiment made on the 7th of April in the present year) was as in fig. 4, indicating three obsolete maxima  $c, d, e$ , and a very sudden diminution of the action at  $b, f$ , the dimensions being as follows:  $Y a = -9.4$ ,  $Y b = +7.1$ ,  $Y c = +12.5$ ,  $Y d = +23.5$ ,  $Y e = +34.0$ ,  $Y f = +41.4$ ,  $Y g = +59.7$ . The paper thus impressed was again re-examined on the 2nd of May, or after twenty-five days, during which interval it had been exposed to free air, but only to feeble and dispersed occasional lights. It was found to have undergone a remarkable change, two distinct white spots having become insulated, or nearly so, at the very extremities of the impressed spectrum, the three maxima above indicated having also become much more distinct, and two new, subordinate ones, having begun to show themselves in the faint traces connecting the spots above mentioned with the main impression. The type of the spectrum in this state was as represented in fig. 5, and the places of the several maxima being as follows:—1st,  $-10.0$ ; 2nd,  $-0.5$ ; 3rd,  $+12.0$ ; 4th,  $+29.0$ ; 5th,  $+40.0$ ; 6th,  $+50$ ; 7th,  $+61.0$ . The terminal spot at the red extremity was nearly equal in diameter to the sun's image; that at the least refracted end, corresponding in place to rays much beyond the last violet, was smaller, but perfectly distinct; and as it constitutes the only instance I have yet encountered of a *definite* ray in this region of the spectrum\*, I have been thus particular in describing the phenomenon.

177. *Common ten-weeks Stock, Matthiola annua.*—The colour imparted by the petals of the *double variety* of this flower† to alcohol (at least when spread on paper, for it is in great measure dormant in the liquid tincture) is a rich and florid rose-red, varying, however, from a fiery tint almost amounting to scarlet, on the one hand, to a somewhat crimson or slightly purplish red on the other, according to the accidents of its preparation, or the paper used. When fresh prepared it is considerably sensitive, an hour or two of exposure to sunshine being sufficient to produce a sensible discolouration, and two or three days entirely to whiten it. This quality is greatly deteriorated by keeping, but papers prepared with it even after eight or ten months, still with patience yield extremely beautiful photographs, several specimens of which in various states of the tincture are submitted for inspection to the meeting. Exposed to the spectrum, the rays chiefly active in operating the discolouration are found to be those extending from the yellow to the less refrangible red, beyond which rays the action terminates abruptly. Above the yellow it degrades rapidly to a minimum in the blue, beyond which it recovers somewhat, and attains a second but much feebler maximum in the violet rays.

\* Since this was written, other cases, extremely remarkable, among the argentine preparations, have presented themselves. See Art. 214.

† That imparted by the single flowers is very much less sensitive, as is also that of the dull red or purplish variety, whether double or single. The most florid red double flowers in the height of their flowering, yield the best colour.

178. Paper stained with the tincture of this flower is changed to a vivid scarlet by acids, and to green by alkalies; if ammonia be used the red colour is restored as the ammonia evaporates, proving the absence of any acid quality in the colouring matter sufficiently energetic to coerce the elastic force of the alkaline gas. Sulphurous acid whitens it, as do the alkaline sulphites; but this effect is transient, and the red colour is slowly restored by free exposure to air, especially with the aid of light, whose influence in this case is the more remarkable, being exactly the reverse of its ordinary action on this colouring principle, which it destroys irrecoverably, as above stated. The following experiments were made to trace and illustrate this curious change.

179. Two photographic copies of engravings taken on paper tinted with this colour were placed in a jar of sulphurous acid gas, by which they were completely whitened, and all traces of the pictures obliterated. They were then exposed to free air, the one in the dark, the other in sunshine. Both recovered, but the former much more slowly than the latter. The restoration of the picture exposed to sun was completed in twenty-four hours, that in the dark not till after a lapse of two or three days.

180. A slip of the stained paper was wetted with liquid sulphurous acid and laid on blotting-paper similarly wetted. Being then crossed with a strip of black paper, it was laid between glass plates and (evaporation of the acid being thus prevented) was exposed to full sunshine. After some time the red colour (in spite of the presence of the acid) was considerably restored in the portion exposed, while the whole of the portion covered by the black paper remained (of course) perfectly white.

181. Slips of paper, stained as above, were placed under a receiver, beside a small capsule of liquid sulphurous acid. When completely discoloured they were subjected (on various occasions, and after various lengths of exposure to the acid fumes from half an hour to many days) to the action of the spectrum; and it was found, as indeed I had expected, that *the restoration of colour was operated by rays complementary to those which destroy it in the natural state of the paper*; the violet rays being chiefly active, the blue almost equally so, the green little, and the yellow, orange, and most refrangible red not at all. In one experiment a pretty well-defined red solar image was developed by the *least* refrangible red rays also, being precisely those for which in the unprepared paper the discolouring action is abruptly cut off. But this spot I never succeeded in reproducing; and it ought also to be mentioned, that, according to differences in the preparation not obvious, the degree of sensibility, generally, of the bleached paper to the restorative action of light differed greatly; in some cases a perceptible reddening being produced in ten seconds, and a considerable streak in two minutes, while in others a very long time was required to produce any effect.

182. The dormancy of this colouring principle, under the influence of sulphurous acid, is well shown by dropping a little weak sulphuric acid on the paper bleached by that gas, which immediately restores the red colour in all its vigour. In like manner alkalies restore the colour, converting it at the same time into green.

183. *Papaver orientale*.—The chemical habitudes of the sulphurous acid render it highly probable that its action, in inducing a dormant state of the colorific principle, consists in a partial deoxidizement, unaccompanied however with disorganization of its molecules. And this view is corroborated by the similar action of alcohol already spoken of; similar, that is, in kind, though less complete in degree. Most commonly, vegetable colours, weakened by the action of alcohol, are speedily restored on the total evaporation of that ingredient. But one remarkable instance of absolute dormancy induced by that agent, has occurred to me in the case of the *Papaver orientale*, a flower of a vivid orange colour, bordering on scarlet, the colouring matter of which is not extractable otherwise than by alcohol, and then only in a state so completely masked, as to impart no more than a faint yellowish or pinkish hue to paper, which it retains when thoroughly dry, and apparently during any length of time without perceptible increase of tint. If at any time, however, a drop of weak acid be applied to paper prepared with this tincture, a vivid scarlet colour is immediately developed, thus demonstrating the continued though latent existence of the colouring principle. On observing this, it occurred to me to inquire whether, in its dormant state, that principle still retained its susceptibility of being acted on by light, since the same powerful and delicate agent which had been shown, in so many cases as to constitute a general law, capable of disorganising and destroying vegetable colours actually developed, might easily be presumed competent to destroy the capacity for assuming colour, in such organic matter as might possess it, under the influence of their otherwise appropriate chemical stimuli. A strip of the paper was therefore exposed for an hour or two to the spectrum, but without any sensible effect, the whole surface being equally reddened by an acid. As this experiment sufficiently indicated the action of light, if any, to be very slow, I next placed a strip, partly covered, in a south-east window, where it remained from June 19 to August 19, receiving the few and scanty sunbeams which that interval of the deplorable summer of 1841 afforded. When removed, the part exposed could barely be distinguished from the part shaded, as a trifle yellower. But on applying acid, the exposed and shaded portions were at once distinguished by the assumption of a vivid red in the latter, the former remaining unchanged.

184. A mezzotinto picture was now pressed on a glazed frame over another portion of the same paper, and abandoned on the upper shelf of a green-house to whatever sun might occur from August 19 to October 19. The interval proved one of almost uninterrupted storm, rain, and darkness. On removal, no appearance whatever of any impressed picture could be discerned, nor was it even possible to tell the top of the picture from the bottom. It was then exposed in a glass jar to the fumes of muriatic acid, when, after a few minutes, the development of the dormant picture commenced, and slowly proceeded, disclosing the details in a soft and pleasing style. Being then laid by in a drawer, with free access of air, the picture again faded, by very slow degrees, and on January 2, 1842, was found quite obliterated. Being then

again subjected to the acid vapour, the colour was reproduced. How often this alternation might have gone on I cannot say, the specimen having been mislaid or destroyed. But a portion of such paper photographically impressed with a stamped pattern, accompanies this communication for the satisfaction of any Member who may wish to try the experiment. The extreme slowness of the action precludes any prismatic analysis of the process, and it cannot be too often repeated *that the use of coloured glasses in such inquiries serves only to mislead.* Of dormant photographic impressions generally, whether slowly developing themselves by lapse of time, or at once revivable by stimuli, as well as of the spontaneous fading and disappearance of such impressions, I shall have more to say hereafter, having encountered several very curious cases of the kind in studying the habitudes of gold, platina, &c. I would here only observe, that a consideration of many such phenomena has led me to regard it as not impossible that the retina itself may be *photographically* impressible by strong lights, and that some at least of the phenomena of visual spectra and secondary colours may arise from the sensorial perception of actual changes in progress in the physical state of that organ itself, subsequent to the cessation of the direct stimulant.

**TURMERIC.—*Further proofs of the continuation of the visible Prismatic Spectrum beyond the extreme Violet.***

185. The action of light on paper coloured with the alcoholic tincture of turmeric is but feeble. If long continued, however, it is whitened in the region of the blue and violet rays, from + 10 to + 43, or thereabouts, the maximum being at + 23.5. The paper browned by carbonate of soda is somewhat more sensitive, especially when wet, in which case an abruptly terminated action is perceptible in the red region, giving rise to a double maximum at - 10.0 and + 22.5, with an intermediate minimum at - 4.0. I should not have thought it necessary, however, to mention this paper, but on account of a remarkable peculiarity in its reflective power, in virtue of which it renders very plainly visible a prolongation of the spectrum beyond the extreme violet, in the region of what I have termed in my last paper, the Lavender rays. As the experiment is easily made, and affords a ready method of rendering visible this part of the spectrum, I shall describe, with some minuteness, the appearances which presented themselves in my experiments, and which seem to place the real existence of those heretofore undescribed luminous rays beyond all reasonable objection, should any doubt have arisen as to the interpretation of the phenomenon described in my former paper (Art. 59.).

186. Paper stained with tincture of turmeric is of a brilliant yellow colour, and in consequence, the spectrum thrown on it, if exposed in the open daylight, is considerably affected in its apparent colours, the blue portion appearing violet, and the violet very pale and faint; but beyond the region occupied by the violet rays is distinctly to be seen a faint prolongation of the spectrum, terminated laterally, like the rest of it, by strait and sharp outlines, and which in this case affects the eye with the sensation of

a pale yellow colour. Comparative measures were carefully taken of the spectrum so prolonged, and of the ordinary spectrum as seen projected on white paper, the results being as follows (see fig. 6.) :—

Length of the spectrum  $Y\ L$  from the fiducial point  $Y$  to the visible termination  $L$ , as seen (with the naked eye) on the turmeric paper; } = 56.6  
corrected for  $\odot$ 's semidiameter. . . . .

Length  $Y\ V$  from the same fiducial point to the visible termination, } = 40.4  
as similarly seen when projected on white paper . . . . .

Prolongation rendered visible by projection of the spectrum on turmeric paper . . . . . } = 16.2

187. The day on which this experiment was first made (May 27, 1841) was serene and clear, but being aware that in certain states of the atmosphere a vertical beam of halo-light passes through the sun, which in a meridional position of that luminary *might* give rise to a perceptible prolongation, both upwards and downwards (though in fact no such prolongation was perceived at the red end), it was often repeated, and always with the same result, on subsequent occasions, whether the sun were on or near the meridian, or otherwise. Comparative trials, also with other yellow papers, fully satisfied me of the cause being traceable to a peculiarity in the colouring material, as to its reflective powers. In particular, a certain paper (No. 1055.) coloured with the juice of *Chryseis californica*, whose tint was almost identical with that of the turmeric paper, only somewhat *brighter*, was tried, and the spectrum measured on this paper was found to terminate precisely at 44.0, i. e. (correcting for semidiameter) at 40.4, the very same as if white paper had been used.

188. To test the matter yet more pointedly, a strip of turmeric paper was fixed on the *Chryseis* paper, so that its edge should bisect the spectrum longitudinally from end to end, the preceding half of the sun's lengthened image being received on the one paper, and the following half on the other. The papers thus arranged were so similar as hardly to be distinguished when simply laid in sunshine, but when illuminated by the spectrum, as above described, the half of it on the turmeric side was plainly seen to extend far beyond the other, as represented in fig. 6.

189. Hitherto I have met with only one other coloured paper which possesses a similar character in respect of its reflective power, and that by no means in so high a degree. To prepare it, the alcoholic tincture of the dark purple dahlia must be alkalized by carbonate of soda. The mixture is vivid green, which is also, at first, the colour of paper stained with it. But this colour changes in about twenty-four hours to a fine yellow, a little inclining to orange, after which it is remarkably permanent, and very little sensible to photographic impression. On this, as on the turmeric paper, the prolongation of the spectrum appears as a pale yellow streak. And if such, rather than lavender or dove-colour, should be the true colorific character of these rays, we might almost be led to believe (from the evident reappearance of redness mingled with

blue in the violet rays) in a repetition of the primary tints in their order, beyond the Newtonian spectrum, and that if by any concentration rays still further advanced in the "chemical" spectrum could be made to affect the eye with a sense of light and colour, that colour would be green, blue, &c., according to the augmented refrangibility.

190. *Cases of negative Photographic Action on Vegetable Tints.*—Among a collection of plants which I made at the Cape of Good Hope, and have succeeded in rearing in England, occurred three species of a genus allied to *Anthericum*, with brilliant yellow flowers in lengthened spikes, and highly characteristic furred anthers, to which I am not botanist enough to assert the correct application of the name *Bulbine*, assigned to them by a friend in Cape Town. Of these three species, two (*Bulbine bisulcata* and . . . . .) yield from the green epidermis of their leaves and flower-stalks a bright yellow juice, which darkens rapidly on exposure to light, changing at the same time to a ruddy brown. Exposed to the spectrum, the less refrangible rays are found inoperative, either in inducing the change of tint, or in preserving that portion of the paper on which they fall from the influence of dispersed light. The negative action commences at the fiducial yellow, is very feeble as far as + 10, where it begins to increase, and is strong at + 23, where the maximum of effect is situated. Hence it degrades more slowly, is still pretty strong at + 60, and may be traced as far as 80, being therefore nearly commensurate with the spectrum impressed on nitro-argentine paper, a range of action unique, so far as my experience goes in vegetable photography. The species experimented on is that which (supposing it undescribed) I should be disposed to call *triangularis*, from the angular section of its long, slender, smooth, solid leaves; which, with the singular character of its juice, may serve to identify the species, my own specimen (a single one) having been destroyed by insects after flowering superbly. The ultimate tint acquired by the juice is a deep brown, to which it also passes in darkness, but much more slowly. The juices of both species, however, have the same photographic characters.

191. *Cheiranthus cheiri*, *Wall-flower*.—A cultivated double variety of this flower, remarkable for the purity of its bright yellow tint, and the abundance and duration of its flowers, yields a juice when expressed with alcohol, from which subsides, on standing, a bright yellow, uniform, finely divided fecula, leaving a greenish yellow transparent liquid, only slightly coloured, supernatant. The fecula spreads well on paper, and is very sensitive to the action of light, but appears at the same time to undergo a sort of chromatic analysis, and to comport itself as if composed of two very distinct colouring principles, very differently affected. The one on which the intensity and sub-orange tint of the colour depends is speedily destroyed, but the paper is not thereby fully whitened. A paler yellow remains as a residual tint, and this, on continued exposure to light, so far from diminishing in tone, slowly darkens to brown. Exposed to the spectrum, the paper is first speedily reduced nearly to whiteness in the region of the blue and violet rays. More slowly, an insu-

lated solar image is whitened at  $-10\cdot 5$ , or in the less refrangible portion of the red, and the impresssd spectrum assumes the type represented in fig. 7, where  $m Y = -10\cdot 5$ ;  $m' Y = +13\cdot 0$ ;  $Y c = +55$ . The exposure continuing, a brown impression begins to be perceived in the midst of the white streak, which darkens very slowly from  $+18\cdot 6$  to  $+42$ . It never attains any great intensity, but presents a singular appearance in the midst of the white train previously eaten out.

192. The juice in question contains gallic acid, and probably tannin, as is evident from its striking a strong black with persalts of iron. The gallic acid itself (whose singular properties, in conjunction with nitrate of silver, have been developed by Mr. TALBOT, as the basis of his all but magical process of the calotype\*) is affected also negatively by light. Paper washed with its spirituous solution and partially covered, being exposed several months in a window, was found pretty strongly darkened in all the exposed portion. The action is too slow for prismatic analysis, and I am far from attributing to the presence of this acid the phenomenon above recorded. It would rather appear as if some portion of a more decidedly negative ingredient analogous to that which exists in the *Bulbine*, were present. As regards the positive ingredient, I may mention here the common Marigold (in which also the colour resides in an insoluble fæcula) as a flower in which the colouring principle is probably identical both with this and with that of the *Corchorus Japonica*, since it comports itself in the very same manner under the spectrum,—is nearly, or quite as sensitive, and is moreover fugitive, even when carefully defended from light, giving photographs which cannot be preserved. Many other flowers also contain in their juices a portion of this identical, or a very similar yellow principle, probably in a state of greater solubility, and thence disposed to the absorption of oxygen. Thus the juice of a fine purely yellow species of *Mimulus*†, if expressed, with or without alcohol, though vividly yellow in the first moments of expression, passes almost instantly to dirty green, and loses its sensibility to light; but if crushed on paper and immediately dried, the petals give a bright yellow stain which agrees in sensibility, and in the type of the impressed spectrum with the *Corchorus*. The *Ferranea undulata*, a dark brown flower, yields, when expressed, a dull green juice, which, spread on paper and dried, turns very speedily blue under the influence of the blue and violet rays of the spectrum; owing to the destruction of this yellow principle, which, mingling with the substratum of blue (itself a much more indestructible tint), gives it its natural tinge of green. A similar destruction, of probably again the same yellow matter, in

\* Preparations of the gallic acid in conjunction with silver, are noticed by me in my former paper as forming a “problematic exception” to my general want of success in procuring at the very outset of my photographic experiments (in February 1839), papers more sensitive than the simple nitrated or carbonated ones. The problematic feature consisted in spontaneous darkening of the papers laid by to dry in the dark, so at least then considered, but really arising doubtless from light incident on them in their preparation. Acetate of silver was used in their preparation.

† *Mimulus Smithii* (Lindl.).

the colour of the American Marigold\*, causes its tint to pass rapidly in sunshine from brown to green, after which continued exposure produces no further change. The yellow colour of fresh bees'-wax and of palm-oil, are also, I doubt not, referable to the same, or a nearly similar colouring matter, both being very speedily bleached by exposure to light.

193. *Viola odorata*.—Chemists are familiar with the colour of this flower as a test of acids and alkalies, for which, however, it seems by no means better adapted than many others; less so, indeed, than that of the *Viola tricolor*, the common purple Iris, and many others which might be named. It offers, in fact, another, and rather a striking instance of the simultaneous existence of two colouring ingredients in the same flower, comporting themselves differently, not only in regard to light but to chemical agents. Extracted with alcohol, the juice of the violet is of a rich blue colour, which it imparts in high perfection to paper. Exposed to sunshine, a portion of this colour gives way pretty readily, but a residual blue, rather inclining to greenish, resists obstinately, and requires a very much longer exposure (for whole weeks indeed) for its destruction, which is not even then complete. Photographic impressions, therefore, taken on this paper, though very pretty, are exceedingly tedious in their preparation, if we would have the lights sharply made out.

194. The residual tint thus outstanding, after long exposure, is turned, not green, but yellow, by alkalies; or, if greenish at first, a very few hours suffice for the destruction of the slight remnant of blue, and the consequent appearance of the yellow colour. Reasoning on this fact, as well as on the action of light above mentioned, it seems highly probable that the tincture in question holds in solution two distinct colouring principles, of which the one (greatly preponderant in quantity) is destructible by light, and either destroyed or turned green by alkalies; the other, indestructible by light, and either naturally yellow in colour or changeable into yellow by alkaline agency.

195. This view of the composite nature of the colour in question receives corroboration from the habits of the alcoholic tincture above mentioned, when rendered green by admixture of carbonate of soda. On making this addition it becomes evident that a large amount of colour has been destroyed; the green tint imparted by it to paper being far less intense than might be expected from the intensity of the original hue, and from the trifling dilution caused by the small quantity of alkaline liquid required to effect the change. What remains is a fine green; but when exposed to light, the blue constituent alone of that green is destroyed, and a residual tint of pure yellow, which is very indestructible by light, is left. Exposure of a slip of such paper to the spectrum proves this change to be operated almost wholly by rays less refrangible than the fiducial yellow. A slight discoloration is perceived in the indigo-blue rays (at about + 30), but the green appears quite inactive.

196. In the case of the purple Iris mentioned above, when turned green by the

\* French Marigold, *Tagetes Patula*.

same reagent, the tint is fuller and richer, as well as, photographically, more sensitive, and the residual yellow less abundant. And in this case the resistance of the tint to rays of its own colour is very strongly marked. The spectral impression consists, in fact, of two portions clearly separated by the whole of the interval occupied by the green and greenish blue rays, conformably to the general remark in Art. 170.

197. *Sparaxis tricolor*? var.—*Stimulating effect of alkalies*.—Among a great many hybrid varieties of this genus, lately forwarded to me from the Cape, occurred one of a very intense purplish brown colour, nearly black. The alcoholic extract of this flower in its liquid state is rich crimson brown. Spread on paper it imparted a dark olive green colour, which proved perfectly insensible to very prolonged action, either of sunshine or the spectrum. The addition of carbonate of soda changed the colour of this tincture to a good green, slightly inclining to olive, and which imparted the same tint to paper. In this state, to my surprise, it manifested rather a high degree of photographic sensibility, and gave very pretty pictures with a day or two of exposure to sunshine. When prepared with the fresh juice there is hardly any residual tint, but if the paper be kept, a great amount of indestructible yellow remains outstanding. The action is confined chiefly to the negative end of the spectrum, the maximum being at  $-8\cdot0$ , and the sensible limits of the impression (corrected for semidiameter) being  $-11\cdot0$  and  $+56\cdot4$ , of which, however, all but the first five or six parts beyond the fiducial yellow show little more than a trace of action. A photograph impressed on this paper is reddened by muriatic acid fumes. If then transferred to an atmosphere of ammonia, and when supersaturated the excess of alkali allowed to exhale, it is fixed, and of a dark green colour. Both the tint and sharpness of the picture, however, suffer in this process.

198. *Red Poppy*—*Papaver Rheum*?.—Among the vegetable colours totally destroyed by light, or which leave no residual tint, at least when fresh prepared, perhaps the two most rich and beautiful are those of the red poppy, and the double purple groundsel (*Senecio splendens*). The former owes its red colour in all probability to free carbonic acid, or some other (as the acetic) completely expelled by drying, for the colour its tincture imparts to paper, instead of red is a fine blue, very slightly verging on slate-blue. But it has by no means the ordinary chemical characters of blue vegetable colours. Carbonate of soda, for instance, does not in the least degree turn the expressed juice green; and when washed with the mixture, a paper results of a light slate-gray, hardly at all inclining to green. The blue tincture is considerably sensitive, and from the richness of its tone and the absence of residual tint, paper stained with it affords photographic impressions of great beauty and sharpness, some of which will be found among the collection submitted with this paper for inspection.

199. *Senecio splendens*.—This flower yields a rich purple juice in great abundance and of surprising intensity. Nothing can exceed the rich and velvety tint of

paper tinted with it while fresh. It is, however, exceedingly insensible to light, and it is only by an exposure continued for many weeks, that it is possible to get a complete photographic impression of a picture on it. Still, when obtained, owing to the whiteness of the ground, the effect is pleasing, and would be beautiful were it not that the general tint suffers somewhat in its tone and softness of surface.

200. The juices of the leaves, stalks, roots, &c. of plants afford a wide and interesting field of photographic inquiry. Those of leaves are for the most part green, and being usually loaded with gum, extractive, &c., are difficult of manipulation. Such as I have tried, which spread well on paper, as the elder, the potatoe, the night-shade, and a few others, proved very sensitive if gathered when just in the perfection of their development, and in full vitality. As the season advances they lose much of their sensibility. There is much uniformity in the action of the spectrum on their colour, in consequence of which I shall content myself with describing the phenomena as exhibited on that of the elder leaf. The type of the impressed spectrum in this case is, as in fig. 8, exhibiting a strong decided maximum of action, giving rise to a nearly insulated solar image at  $-11\cdot 5$ , or almost at the extremity of the red rays. The colour of this image was a pale yellowish pink or flesh colour ; from thence the action is feeble, with two subordinate minima (at  $-5\cdot 0$ ,  $+6\cdot 8$ ), with a slight intermediate maximum at  $0\cdot 0$ , and beyond these (or about the termination of the green) the action again increases ; reaches another maximum at  $+20\cdot 0$ , after which it declines gradually, and beyond  $+45$  ceases to be traceable. Photographic pictures may be taken readily on such papers, half an hour in good sun sufficing ; but the glairy nature of the juices prevents their being evenly tinted, and spoils their beauty\*.

201. The ruddy tint which comes out when the green is destroyed by light, is in all probability that which gives the whole colour to sere and withered leaves, whether simply disclosed by the destruction of the green which masked it in the live state of the leaf, or matured by exposure to light during the whole season, either out of the elements of the green colouring matter destroyed, or from the other juices of the vegetable. It deserves to be noticed in connexion with this, that all the lively vegetable greens have a large portion of red in their composition, and are in fact dichromatic. A good example of such a colour is a solution of sap-green, which, used as a prism, is seen to transmit both red and green rays, separating them by a broad interval which increases as the thickness or density of the solution is increased ; the red ultimately preponderating, and the green being extinguished. If we view a garden or shrubbery through a glass of a pure and deep red colour, every shrub, such as the laurel, of a lively and brilliant foliage, and especially green grass, will appear scarlet. Under such circumstances, a grass-plot, seen in contrast with a gravelled walk, shows as light on darkness, contrary to their habitual order of illumination. So great is the quantity of extreme red light reflected by a green sward, as actually

\* I have not operated on chlorophyle (the green colouring matter of leaves) in a state of purity, owing to the nicety required in its preparation.

to appear bright in opposition to clear blue sky seen through the same glass in the quarter of the heavens opposed to the sun, and that at noon day. The aspect of nature, indeed, when viewed through coloured glasses, is fraught with curious and interesting matter of optical remark ; but to give them their full effect they must not be merely applied to one eye for a few moments, as in the use of Claude Lorraine glasses. They should be worn as spectacles, both eyes being used, all lateral light carefully excluded by black velvet fringes, and their use continued till the pupil is fully dilated and the eye familiarized with the intensity and tone of the illumination. So used, not only are the ordinary relations of all lights and colours strangely and amusingly deranged, but contrasts arise between colours naturally the most resembling, and resemblances between those naturally the most opposed. We become aware of elements in the composition of tints we should otherwise never have suspected, and the singularities of idio-chromic vision which seem so puzzling, when related, cease to be matter of any surprise\*.

202. I shall conclude this part of my subject by remarking on the great number and variety of substances which, now that attention is drawn to the subject, appear to be photographically impressible. It is no longer an insulated and anomalous affection of certain salts of silver and gold, but one which, doubtless, in a greater or less degree pervades all nature, and connects itself intimately with the mechanism by which chemical combination and decomposition is operated. The general instability of organic combinations might lead us to expect the occurrence of numerous and remarkable cases of this affection among bodies of that class, but among metallic and other elements inorganically arranged, instances enough have already appeared, and more are daily presenting themselves, to justify its extension to all cases in which chemical elements may be supposed combined with a certain degree of laxity, and so to speak, in a state of tottering equilibrium. There can be no doubt that the process, in a great majority if not all the cases which have been noticed among inorganic substances, is a deoxidizing one, so far as the more refrangible rays are concerned. It is obviously so in the cases of gold and silver. In that of the bichromate of potash it is most probable that an atom of oxygen is parted with, and so of many others. A beautiful example of such deoxidizing action on a non-argentine compound has lately occurred to me in the examination of that interesting salt, the ferroesquicyanuret of potassium, described by Mr. SMEE in the Philosophical Magazine, No. 109, September 1840, and which he has shown how to manufacture in abundance and purity by voltaic action on the common, or yellow ferrocyanuret. In this process nascent oxygen is absorbed, hydrogen given off, and the characters of the result-

\* The late celebrated optician Mr. TROUGHTON, who was a remarkable instance of this sort of vision, informed me that he could not distinguish the scarlet coats of a regiment of soldiers from the green turf on which they were drawn up, nor ripe cherries from the leaves of the tree which bore them. His eyes, however, were perfectly sensible to rays of every refrangibility *as light*, but the spectrum afforded him only the sensations of two *colours*, which he termed blue and yellow ; pure red and pure yellow rays exciting in his mind the same sensation.

ing compound in respect of the oxides of iron, forming as it does Prussian blue with protosalts of that metal, but producing no precipitate with its persalts, indicate an excess of electro-negative energy, a disposition to part with oxygen, or, which is the same thing, to absorb hydrogen (in the presence of moisture), and thereby to return to its pristine state, under circumstances of moderate solicitation, such as the affinity of protoxide of iron (for instance) for an additional dose of oxygen, &c.

203. Paper simply washed with a solution of this salt is highly sensitive to the action of light. Prussian blue is deposited (the base being necessarily supplied by the destruction of one portion of the acid, and the acid by the decomposition of another). After half an hour or an hour's exposure to sunshine, a very beautiful negative photograph is the result, to fix which all that is necessary is to soak it in water, in which a little sulphate of soda is dissolved, to ensure the fixity of the Prussian blue deposited. While dry, the impression is dove-colour or lavender blue, which has a curious and striking effect on the greenish yellow ground of the paper produced by the saline solution. After washing, the ground colour disappears, and the photograph becomes bright blue on a white ground. If too long exposed it gets "oversunned," and the tint has a brownish or yellowish tendency, which however is removed in fixing: but no increase of intensity beyond a certain point is obtained by continuance of exposure.

204. Prismatic examination of this process demonstrates the remarkable and valuable fact, that the decomposition of the salt and deposit of Prussian blue is due to the action of the blue and violet rays, the less refrangible rays below the blue having absolutely no influence either to exalt or diminish the effect. The limits of action are about  $+18^{\circ}0$  and  $+61^{\circ}0$ , fading insensibly both ways. The greatest intensity of action is at  $+38$ . A feebler maximum occurs at  $+23$ . The intensity of the impression is much increased by washing with acidulated water, still more if it hold in solution a little persalt of iron, but in this case the ground, if not very carefully defended from light, is blue.

205. If a solution of this salt, mixed with perchloride of iron in a certain proportion, be washed over paper somewhat bibulous and exposed to the spectrum, a copious and intense deposit of Prussian blue takes place over the region indicated in the last article. But it does not terminate there. On the contrary, the action is continued downwards in the spectrum, not only down to and beyond the extreme red rays, but far below, *down to the very end of the thermic spectrum* (as far as the spot called  $\delta$  in Art. 136, and even with some traces of the more remote spot  $\epsilon$ ). The formation of the deposited colour in this region is accompanied with very singular phenomena, referable obviously to the heat developed by the thermic spectrum. Soon after the blue train,  $a\ b$ , fig. 9, in the positive region of the spectrum is formed, and has begun to acquire some intensity, an oval  $\alpha$ , blunt at one extremity and pointed at the other, and of a dark brown colour, begins to appear. It enlarges rapidly, and at the same time throws forth a projection  $\beta$ , indicating the action of that portion of the

thermic spectrum so characterized in Art. 136. It also acquires a whitish narrow border, indicated by the dotted line, and very conspicuous on the green ground of the paper. The action continuing, the spot  $\gamma$  is marked out by the extension of the border in that direction, soon after which the spot appears, in brown. Lastly appears  $\delta$  with feeble traces of further irregular and interrupted action. Measurements of these spots as they appear, leave no doubt of their identity in situation with the thermic spots  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  of Art. 136, and that they are referable to the drying of the paper is shown by the fact, that a film of the liquid dried in a porcelain saucer changes from green to dark brown at a definite point of dryness. Moreover, on wetting the paper, the brown spots disappear, and in their place we find a train of Prussian blue, of varying intensity, but of *uniform breadth* (not swelling and contracting, as is the case with the heat-spots formed by simple drying, and *therefore* obviously due to *direct* radiation), and terminating in two insulated and tolerably well-defined circular spots or solar images, holding precisely the places of  $\gamma$  and  $\delta$  (viz. at  $-35.7$  and  $-45.1$ ).

206. If in lieu of the perchloride of iron, we substitute a solution of that curious salt the *ammonio-citrate of iron*, the photographic effects are among the most various and remarkable that have yet offered themselves to our notice in this novel and fertile field of inquiry. The two solutions mix without causing any precipitate, and produce a liquid of a brown colour, which washed over paper is green (being strongly dichromatic). If this be done under the prism, the action of the spectrum is almost instantaneous, and most intense. A copious and richly coloured deposit of Prussian blue is formed over the whole of the blue, violet, and extra-spectral rays in that direction, extending downwards (with rapid graduation) almost to the yellow. If arrested when the blue is most intense and thrown into water, the impression is fixed, as in the accompanying specimen (see fig. 10.). But if the action of the light be continued, strange to say, the blue and violet rays begin to destroy their own work. A *white oval* makes its appearance in the most intense part of the blue (fig. 11.), which extends rapidly upwards and downwards. At a certain point of the action, the upper or more refrangible extremity of the white impression exhibits a semicircular termination, beyond which is a distinct and tolerably well-defined *conjugate image*, or insulated circular white spot, whose centre is situated far beyond the extreme visible violet.

207. If paper washed over with the mixed solution in question is exposed wet to sunshine, it darkens to a livid purple and rapidly whitens again. If the exposure be continued, the white again darkens gradually to a brownish violet hue. But in the shade it slowly resumes its original tint, after which it is again and again susceptible of the same round of action. The most singular and apparently capricious varieties of coloration and discoloration however arise (as is so frequently the case in photographic experiments) from different dosage of ingredients, order of washes, &c., so as to make the study of the phenomena in a high degree complicated\*. A certain adjustment

\* The whitening is very obviously due to the deoxidation of the precipitated Prussian blue and the formation

of proportions gives an exquisite and highly sensitive *positive* photographic paper; another, a negative one, in which the impression of light, feeble at first, is strongly brought out afterwards by an additional wash of the ferroesquicyanuret, &c.

208. The ordinary ferrocyanuret (the yellow salt), though not nearly so sensible to photographic action, is yet far from inert. In my former paper I have noticed its property of fixing against the further action of light, and ultimately destroying, photographic impressions on argentine papers. In conjunction also with preparations of silver, it has been made by Mr. HUNT the basis of a highly sensitive photographic paper. Its *habitudes per se* are, however, not a little remarkable. Paper simply washed with its fresh solution and exposed to the spectrum, slowly receives a deposit of Prussian blue over the region of the blue, violet, and "lavender" rays: but this never becomes intense; another series of changes commencing, indicated by the formation of a violet-coloured streak within the blue, just where the violet itself is most intense in the spectrum. If the solution be very feebly acidulated with sulphuric acid, the first portion only of the spectral impression (from + 13.3 to + 20.0) is blue, the whole of the remainder (extending to + 51) snuff brown. The dose of acid being increased, the exposure prolonged, and the liquid plentifully supplied, a green thermic impression is produced by the less refrangible rays, in which the spots  $\alpha$ ,  $\beta$ ,  $\gamma$  are very distinct, and lie exactly (by measure) in their proper places. This impression continues as far as the zero point, where it begins to pass into blue, and graduates insensibly into the photographic spectrum, which attains its maximum of blue at + 25, and is thence prolonged onwards as a dull bluish streak on a brown ground, somewhat broader than itself, and projecting like a border on both sides.

209. If paper be washed with a solution of ammonio-citrate of iron and dried, and then a wash passed over it of the yellow ferrocyanuret of potassium, there is no immediate formation of true Prussian blue, but the paper rapidly acquires a violet purple colour, which deepens after a few minutes, as it dries, to almost absolute blackness. In this state it is a positive photographic paper of high sensibility, and gives pictures of great depth and sharpness, but with this peculiarity, that they darken again spontaneously on exposure to air in darkness, and are soon obliterated. The paper, however, remains susceptible to light and capable of receiving other pictures, which in their turn fade, without any possibility (so far as I can see) of arresting them; which is to be regretted, as they are very beautiful, and the paper of such easy preparation. If washed with ammonia or its carbonate, they are for a few moments entirely obliterated, *but presently reappear, with reversed lights and shades*. In this state they are fixed, and the ammonia, with all that it will dissolve, being removed by washing in water, their colour becomes a pure Prussian blue, which deepens much by keeping. If the solutions be mixed there results a very dark violet-coloured

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of the proto-ferrocyanuret of iron; the resumption of colour in the shade, to the re-oxidizement of this compound, which is well known to absorb oxygen from the air with avidity. Simple Prussian blue, however, is not whitened by the violet rays. Its state must be peculiar. (See Postscript.)

ink, which may be kept uninjured in an opaque bottle, and will readily furnish, by a single wash, at a moment's notice, the positive paper in question, which is most sensitive when wet.

210. It seems at first sight natural to refer these curious and complex changes to the instability of the cyanic compounds, and that this opinion is to a certain extent correct, is proved by the photographic impressions described in Arts. 204 and 209, where no iron is added beyond what exists in the ferrocyanic salts themselves. Nevertheless the following experiments abundantly prove that in several of the changes above described, the *immediate action* of the solar rays is not exerted on these salts, but on the iron contained in the ferruginous solution added to them, which it deoxidizes or otherwise alters, thereby presenting it to the ferrocyanic salts in such a form as to precipitate the acids in combination with the peroxide or protoxide of iron, as the case may be. To make this evident, all that is necessary is *simply to leave out the ferrocyanate* in the preparation of the paper, which thus becomes reduced to a simple washing over with the ammonio-citric solution. Paper so washed is of a bright yellow colour, and is apparently little, but in reality highly sensitive to photographic action. Exposed to strong sunshine for some time indeed, its bright yellow tint is dulled into an ochrey hue, or even to gray, but the change altogether amounts to a moderate per centage of the total light reflected, and in short exposures is such as would easily escape notice. Nevertheless, if a slip of this paper be held for only four or five seconds in the sun (the effect of which is quite imperceptible to the eye), and when withdrawn into the shade be washed over with the ferrosesquicyanate of potash, a considerable deposit of Prussian blue takes place on the part sunned, and none whatever on the rest, so that on washing the whole with water, a pretty strong blue impression is left, demonstrating the reduction of iron in that portion of the paper to the state of protoxide. The effect in question is not, it should be observed, peculiar to the ammonio-citrate of iron. The ammonio- and potasso-tartrate fully possess, and the perchloride *exactly neutralized* partakes of the same property: but the experiment is far more neatly made and succeeds better with the other salts.

211. If a long strip of paper, prepared as in the last article, be marked off into compartments and subjected to graduated exposure to sunshine, so that the times of exposure in each succession shall form an arithmetical progression of 1<sup>m</sup>, 2<sup>m</sup>, &c., and when withdrawn washed over as aforesaid with the ferrosesquicyanuret and rinsed in water, the blue deposit is found to increase with the time of exposure up to a very deep and full colour, after which its total intensity, so far from increasing, diminishes, and at length almost vanishes. Again, if a slip of the same paper be exposed a long while to the spectrum, the whole impression consists in a feeble ochrey-brown streak, extending over the region of the blue, violet and lavender rays as far as about + 55. But on the application of the cyanic solution (in the shade) a most intense blue spectrum is developed over the whole of the more refrangible region, in the interior of which the blue colour appears to have been, as it were, eaten away,

leaving a white oval, as in the specimen annexed ; precisely the same phenomenon, in short, as would have been produced under the spectrum had the two liquids acted in conjunction. And this white portion comports itself under the influence of water or air, just as it would have done had it been produced under such joint action ; i. e. it gradually turns blue till it is no longer distinguishable from the rest of the spectrum. It is also blued by ammonia, just as the positive paper of Art. 210, after bleaching, would be, &c. In short, it is evident that we have succeeded in separating the final action described in that article into two distinct steps or stages, the photographic influence being confined to the first, and the ferrosesquicyanate acting as a mere precipitant on the nascent compounds resulting from that influence.

212. In order to ascertain whether any portion of the iron in the double ammoniacal salt employed had really undergone deoxidation, and become reduced to the state of protoxide as supposed, I had recourse to a solution of gold, exactly neutralized by carbonate of soda. The proto-salts of iron, as is well known to chemists, precipitate gold in the metallic state. The effect proved exceedingly striking, issuing in a process no wise inferior in the almost magical beauty of its effect to the calotype process of Mr. TALBOT, which in some respects it nearly resembles, with this advantage, as a matter of experimental exhibition, that the disclosure of the dormant image does not require to be performed in the dark, being not interfered with by moderate daylight. As the experiment will probably be repeated by others, I shall here describe it *ab initio*. Paper is to be washed with a moderately concentrated solution of ammonio-citrate of iron, and dried. The strength of the solution should be such as to dry into a good yellow colour, not at all brown. In this state it is ready to receive a photographic image, which may be impressed on it either from nature in the camera-obscura, or from an engraving on a frame in sunshine. The image so impressed, however, is very faint, and sometimes hardly perceptible. The moment it is removed from the frame or camera, it must be washed over with a neutral solution of gold of such strength as to have about the colour of sherry wine. Instantly the picture appears, not indeed at once of its full intensity, but darkening with great rapidity up to a certain point, depending on the strength of the solutions used, &c. At this point nothing can surpass the sharpness and perfection of detail of the resulting photograph. To arrest this process and to fix the picture (so far at least as the further agency of *light* is concerned), it is to be thrown into water very slightly acidulated with sulphuric acid and well soaked, dried, washed with hydrobromate of potash, rinsed, and dried again.

213. Such is the outline of a process to which I propose applying the name of *Chrysotype*, in order to recal by similarity of structure and termination the *Calotype* process of Mr. TALBOT, to which in its general effect it affords so close a parallel. Being very recent, I have not yet (June 10, 1842) obtained a complete command over all its details, but the termination of the Session of the Society being close at hand, I have not thought it advisable to suppress its mention. In point of *direct*

sensibility, the Chrysotype paper is certainly inferior to the Calotype; but it is one of the most remarkable peculiarities of gold as a photographic ingredient, that *extremely feeble impressions once made by light, go on afterwards darkening spontaneously, and very slowly, apparently without limit, so long as the least vestige of unreduced chloride of gold remains in the paper*\*. To illustrate this curious and (so far as applications go) highly important property, I shall mention (incidentally) the results of some experiments made during the late fine weather, on the habitudes of gold in presence of oxalic acid. It is well known to chemists that this acid heated with solutions of gold precipitates the metal in its metallic state; it is upon this property that BERZELIUS has founded his determination of the atomic weight of gold. Light, as well as heat, also operates this precipitation; but to render it effectual, several conditions are necessary:—1st, the solution of gold must be neutral, or at most *very* slightly acid; 2nd, the oxalic acid must be added in the form of a neutral oxalate; and 3rdly, it must be present in a certain considerable quantity, which quantity must be greater, the greater the amount of free acid present in the chloride. Under these conditions, the gold is precipitated by light as a black powder if the liquid be in any bulk, and if merely washed over paper a stain is produced, which, however feeble at first, under a certain dosage of the chloride, oxalate, and free acid, goes on increasing from day to day and from week to week, when laid by in the dark, and especially in a damp atmosphere, till it acquires almost the blackness of ink; the unsunned portion of the paper remaining unaffected, or so slightly as to render it almost certain that what little action of the kind exists is due to the effect of casual dispersed light incident in the preparation of the paper. I have before me a specimen of paper so treated, in which the effect of thirty seconds exposure to sunshine was quite invisible at first, and which is now of so intense a purple as may well be called black, while the unsunned portion has acquired comparatively but a very slight brown. And (which is not a little remarkable, and indicates that in the time of exposure mentioned the *maximum* of effect was attained) other portions of the same paper exposed in graduated progression for longer times, viz. 1<sup>m</sup>, 2<sup>m</sup>, and 3<sup>m</sup>, are not in the least perceptible degree darker than the portion on which the light had acted during thirty seconds only.

214. The very remarkable phenomenon described in Art. 208. of a second darkening, different in character and colour, coming on after the bleaching effect of solar light has been fully completed, is not without a parallel among the argentine compounds. I refer to the action of the hydriodic salts on argentine papers completely blackened by exposure to sunshine, an action imperfectly described in § 5. of my former paper (Art. 94 *et seq.*), and signalized as to one of its most striking peculiarities in Note 2, Art. 129. of that communication. To study the phenomena of this action in their simplest form, a paper prepared without iodine, and of a positive

\* Subsequent experiments have convinced me that this property cannot be taken advantage of to increase the intensity of the chrysotype impression, however it may be available in other processes. Note added during the printing, J. F. W. H.

character is required. The simplest and most convenient is that prepared by Mr. HUNT with one wash of muriate of ammonia, two of nitrate of silver\*, and exposure to sunshine. With such paper (obligingly furnished me by Mr. HUNT himself) I made the following experiments.

215. Exposed to the spectrum and washed with a solution of hydriodate of potash too weak fully to excite it†, two contrary actions were produced by the rays above and below the zero point or mean yellow. By the former the paper began to be bleached at a point distant + 26·5 parts from the zero, from which point the bleaching extended gradually upwards to a considerable distance, and downwards to the circumference of a semicircle, having that point for a centre. By the latter the paper was darkened (at least in comparison with its general surface, which, purposely subjected to dispersed light, had begun to lose much of its original intense blackness), the darkness spreading also upwards and downwards: upwards till it passed the zero point, and nearly or quite attained the semicircle above mentioned; and downwards to about - 19, or - 20 parts. As the paper dried the action seemed to be suspended. It became therefore necessary to renew the hydriodic wash, and thereby to increase the actual quantity of that salt present on the paper. Both actions grew more intense, but the bleaching effect most so. A perfect semicircle and long cometic train, *c, d*, fig. 12, No. 1, was produced, within which space the blackness of the paper was totally destroyed, and replaced by white or rather very pale yellow. The hydriodic washes being again and again renewed, the darkness at first produced in the lower part of the spectrum began to give way, and was slowly replaced by a very feeble bleaching, which at length extended very far indeed below the extreme red rays, and upwards to join the semicircle *C* fig. 12, No. 2, which had by this time assumed an outline perfectly sharp and well-defined, having its centre on the original point + 26·5 of its commencement. But *within* this semicircle and its train, remarkable changes were observed to be all the while in progress. First, a somewhat dark, and greyish or brownish, perfectly circular and well-defined solar image arose, its diameter being somewhat less than that of the semicircular terminations, *so as to leave a clear and distinct white border all around it*, as represented by the dotted line in fig. 12, No. 2. Shortly after the complete formation of this spot, i. e. after its circular outline could be distinctly traced all round, it began to extend itself upwards into an oval or tailed form, but preserving its circular shape below and maintaining the white border inviolate, assuming at the same time a brownish yellow colour which gradually deepened, but never became intense. At the same time a very remarkable change was observed to take place in the reflective (or absorbent) powers of the paper in this region. The violet-coloured end of the spectrum, which hitherto had been distinctly seen as usual occupying the space from + 30 to + 40·6, became quite indiscernible, while on the other hand the blue rays adjoining became reflected with such co-

\* Muriate of ammonia forty grains, water four ounces; nitrate of silver sixty grains, water one ounce.

† Ioduret of potassium sixty grains, water one ounce.

piousness as to terminate the spectrum by a well-defined semicircle *e*, fig. 12, No. 3, and to give to the whole portion *c e* the appearance of a brilliant and purely blue spot. Finally, after long-continued action, the interior browned oval above-mentioned was found to have been prolonged into a figure of the form No. 4, fig. 12 (distinctly seen at the *back* of the paper), of which the termination by a narrow neck and circular enlargement indicates the definite action of a ray much further removed along the axis of the spectrum. Washing with water at once obliterates this part of the phenomenon, destroys the brown colour, and leaves simply the bleached *cometic train*, in singularly striking contrast with the dark ground of the paper. Specimens of the spectrum itself are subjoined for inspection.

216. The black positive paper used in the above experiment (which has been often repeated with the same results) contains free nitrate of silver. If this be washed out, the darkening at the lower end of the spectrum is not produced, but in its place the feeble subsequent bleaching in the region above-mentioned commences at once. And if besides washing with mere water, the paper be subsequently washed with a neutral hyposulphite to remove all chloride of silver, it is reduced to a state of perfect insensibility. It is therefore to this latter element that the direct action of the bleaching rays is to be referred. A few months' keeping also destroys the positive sensibility of the paper in question entirely.

J. F. W. HERSCHEL.

*Collingwood,*  
*June 13, 1842.*

*Postscript added August 29, 1842.*

217. I gladly avail myself of the permission accorded by the President and Council to append to this communication, in the form of a Postscript, some additional facts illustrative of the singular properties of iron as a photographic ingredient, which have been partially developed in the latter articles of it, as well as an account of some highly interesting photographic processes dependent on those properties, which the superb weather we have lately enjoyed has enabled me to discover, as also to describe a better method of fixing the picture, in the process to which I have given the name of *Chrysotype*; that described in Art. 212. proving insufficient. The new method (in which the hydriodate is substituted for the hydrobromate of potash) proves perfectly effectual; pictures fixed by it not having suffered in the smallest degree, either from long exposure to sunshine, or from keeping; alone, or in contact with other papers. It is as follows:—As soon as the picture is satisfactorily brought out by the auriferous liquid (Art. 212.) it is to be rinsed in spring water, which must be three times renewed, letting it remain in the third water five or ten minutes. It is then to be blotted off and dried, after which it is to be washed on both sides with a somewhat

weak solution of hydriodate of potash. If there be any free chloride of gold present in the pores of the paper, it will be discoloured, the lights passing to a ruddy brown; but they speedily whiten again spontaneously, or at all events, on throwing it (after lying a minute or two) into fresh water, in which, being again rinsed and dried, it is now perfectly fixed.

218. If paper prepared as above recommended for the chrysotype, either with the ammonio-citrate or ammonio-tartrate of iron, and impressed, as in that process, with a latent picture, be washed with nitrate of silver instead of a solution of gold, a very sharp and beautiful picture is developed, of great intensity. Its disclosure is not instantaneous; a few moments elapse without apparent effect; the dark shades are then first touched in, and by degrees the details appear, but much more slowly than in the case of gold. In two or three minutes, however, the maximum of distinctness will not fail to be attained. The picture may be fixed by the hyposulphite of soda, which alone, I believe, can be fully depended on for fixing argentine photographs.

219. *Cyanotype*.—If a nomenclature of this kind be admitted (and it has some recommendations), the whole class of processes in which cyanogen in its combinations with iron performs a leading part, and in which the resulting pictures are blue, may be designated by this epithet. The varieties of cyanotype processes seem to be innumerable, but that which I shall now describe deserves particular notice, not only for its pre-eminent beauty while in progress, but as illustrating the peculiar power of the ammoniacal and other persalts of iron above mentioned to receive a latent picture, susceptible of development by a great variety of stimuli. This process consists in simply passing over the ammonio-citratized paper on which such a latent picture has been impressed, *very sparingly and evenly*, a wash of the solution of the common yellow ferrocyanate (prussiate) of potash\*. The latent picture, if not so faint as to be quite invisible (and for this purpose it should not be so), is negative. As soon as the liquid is applied, which cannot be in too thin a film, the negative picture vanishes, and by very slow degrees is replaced by a positive one of a violet-blue colour on a greenish yellow ground, which at a certain moment possesses a high degree of sharpness and singular beauty and delicacy of tint. If at this instant it be thrown into water, it passes immediately to Prussian blue, losing at the same time, however, much of its sharpness, and sometimes indeed becoming quite blotty and confused. But if this be delayed, the picture, after attaining a certain maximum of distinctness, grows rapidly confused, especially if the quantity of liquid applied be more than the paper

\* Vulgarly, and in my opinion very conveniently and *correctly* so called, according to the true intent and meaning of SCHEELE. Trivial names for common objects are to be maintained and defended on principles far more general than systematic nomenclature. For this reason I trust never to see the name muriatic give way to hydrochloric, or nitric thrust aside for azotic acid. The *prussic acid* is that acid, whatever it be, which, united with oxide of iron as a base, forms *Prussian blue*, from which remarkable compound the whole history of cyanogen originated. The now ascertained existence of another ferrocyanate makes this recurrence to a trivial name for the vulgar one more necessary.

can easily and completely absorb, or if the brush in applying it be allowed to rest on, or be passed twice over any part. The effect then becomes that of a coarse and ill-printed wood-cut, all the strong shades being run together, and a total absence prevailing of half lights.

220. To prevent this confusion, gum-arabic may be added to the prussiated solution, by which it is hindered from spreading unmanageably within the pores of the paper, and the precipitated Prussian blue allowed time to agglomerate and fix itself on the fibres. By the use of this ingredient also, a much thinner and more equable film may be spread over the surface ; and *when perfectly dry*, if not sufficiently developed, the application may be repeated. By operating thus I have occasionally (though rarely) succeeded in producing pictures of great beauty and richness of effect, which they retain (if not thrown into water) between the leaves of a portfolio, and have even a certain degree of fixity—fading in a strong light and recovering their tone in the dark. The manipulations of this process are, however, delicate, and complete success is comparatively rare.

221. If sulphocyanate of potash be added to the ammonio-citrate or ammonio-tartrate of iron, the peculiar red colour which that test induces on persalts of the metal is not produced, but appears at once on adding a drop or two of dilute sulphuric or nitric acid. This circumstance, joined to the perfect neutrality of these salts, and their power, in such neutral solution, of enduring, undecomposed, a boiling heat, contrary to the usual habitudes of the peroxide of iron\*, together with their singular transformation by the action of light to proto-salts, in apparent opposition to a very strong affinity, has, I confess, inclined me to speculate on the possibility of their ferruginous base existing in them, not in the ordinary form of peroxide, but in one isomeric with it. The non-formation of Prussian blue, when their solutions are mixed with prussiate of potash (Art. 209.), and the formation in its place of a deep violet-coloured liquid of singular instability under the action of light, seems to favour this idea. Nor is it altogether impossible that the peculiar “prepared” state superficially assumed by iron under the influence of nitric acid, first noticed by KEIR, and since made the subject of experiment by M. SCHÖNBEIN and myself†, may depend on a change superficially operated on the *iron itself* into a new metallic body isomeric with iron, unoxidable by nitric acid, and which may be considered as the radical of that peroxide which exists in the salts in question, and possibly also of an isomeric protoxide. A combination of the common protoxide with the isomeric peroxide, rather than with the same metal in a simply higher stage of oxidation, would afford a not unpleasing notion of the chemical nature of that peculiar intermediate oxide to which the name of “Ferroso-ferric” has been given by BERZELIUS. If (to render my meaning more clear) we for a moment consent to designate such an isomeric form of iron by the name siderium, the oxide in question might be regarded as a sideriate of iron. Both

\* See my paper on this subject in Philosophical Transactions, cxi. p. 293.

† See Annales de Chimie, tom. liv. p. 87.

phosphorus and arsenic (bodies remarkable for sesqui-combinations) admit isomeric forms in their oxides and acids\*. But to return from this digression.

222. If to a mixture of ammonio-citrate of iron and sulphocyanate of potash a small dose of nitric acid be added, the resulting red liquid spread on paper spontaneously whitens in the dark. If more acid be added till the point is attained when the discolouration begins to relax, and the paper when dry retains a considerable degree of colour, it is powerfully affected by light, and receives a positive picture with great rapidity, which, like the guaiacum impression noticed in Art. 154, appears at the back of the paper with even more distinctness than on its face. The impression, however, is pallid; fades on keeping, nor am I acquainted at present with any mode of fixing it.

223. If paper be washed with a mixture of the solutions of ammonio-citrate of iron and ferrosesquicyanate of potash, so as to contain the two salts in about equal proportions, and being then impressed with a picture, be thrown into water and dried, a negative blue picture will be produced agreeably to what is stated in Art. 154. This picture I have found to be susceptible of a very curious transformation, preceded by total obliteration. To effect this it must be washed with solution of proto-nitrate of mercury, which in a little time entirely discharges it. The nitrate being thoroughly washed out and the picture dried, a smooth iron is to be passed over it, somewhat hotter than is used for ironing linen, but not sufficiently so to scorch or injure the paper. The obliterated picture immediately reappears, not blue, but brown. If kept for some weeks in this state between the leaves of a portfolio, in complete darkness, it fades, and at length almost entirely disappears. But what is very singular, a fresh application of the heat revives and restores it to its full intensity.

224. This curious transformation is instructive in another way. It is not operated by light, at least not by light alone. *A certain temperature* must be attained, and that temperature suffices in total darkness. Nevertheless, I find that on exposing to a very concentrated spectrum (collected by a lens of short focus) a slip of paper duly prepared as above (that is to say, by washing with the mixed solutions, exposure to sunshine, washing, and discharging the uniform blue colour so induced as in the last article), its whiteness is changed to brown over the whole region of the red and orange rays, *but not beyond* the luminous spectrum. Three conclusions seem unavoidable;—1st, that it is the heat of these rays, not their light, which operates the change; 2ndly, that this heat possesses a peculiar chemical quality which is not possessed by the purely calorific rays outside of the visible spectrum though far more intense; and, 3rdly, that the heat radiated from obscurely hot iron, abounds especially in rays analogous to those of the region of the spectrum above indicated. And there are the very same conclusions derived from the experiments on guaiacum in Art. 158—160.

\* The latter from the late experiments and remarks of Rose on the vitreous state of the arsenious acid and its luminosity in crystallizing from acid solutions.

225. Whatever be the state of the iron in the double salts in question, its reduction by blue light to the state of protoxide is indicated by many other reagents. If, for example, a slip of paper, prepared with the ammonio-citrate and partially sunned, be washed, when withdrawn, with bichromate of potash, the bichromate is deoxidized and precipitated on the sunned portion, just as it would be if directly exposed to the sun's rays. Every reagent in short which is susceptible of being deoxidized, wholly or in part, by contact with the protoxide of iron, is so also by contact with the sunned paper. Taking advantage of this property, I have been enabled to add another and very powerful element to the list of photographic ingredients.

226. *Photographic Properties of Mercury.*—This element is mercury. As an agent in the Daguerreotype process, it is not, strictly speaking, photographically affected. It operates there only in virtue of its readiness to amalgamate with silver, properly prepared to receive it. That it possesses *direct* photographic susceptibility, however, in a very eminent degree, is proved by the following experiment. Let a paper be washed over with a weak solution of periodide of iron, and when dry with a solution of proto-nitrate of mercury. A bright yellow paper is produced, which (if the right strength of the liquids be hit) is exceedingly sensitive while wet, darkening to a brown colour in a very few seconds in the sunshine. Withdrawn, the impression fades rapidly, and the paper in a few hours recovers its original colour. In operating this change of colour the whole spectrum is effective, with the exception of the thermic rays beyond the red.

227. Proto-nitrate of mercury simply washed over paper is slowly and feebly blackened by exposure to sunshine. And if paper be impregnated with the ammonio-citrate, already so often mentioned, partially sunned, and then washed with the proto-nitrate, a reduction of the latter salt, and consequently blackening of the paper takes place very slowly in the dark over the sunned portion, to nearly the same amount as in the direct action of the light on the simply nitrated paper.

228. But if the mercurial salt be subjected to the action of light in contact with the ammonio-citrate, or tartrate, the effect is far more powerful. Considering, at present, only the citric double-salt, a paper prepared by washing first with that salt and then with the mercurial proto-nitrate (drying between) is endowed with considerable sensibility, and darkens to a very deep brown, nay to complete blackness, on a moderate exposure to good sun. Very sharp and intense photographs of a negative character may be thus taken. They are however difficult to *fix*. The only method which I have found at all to succeed, has been by washing them with bichromate of potash and soaking them for twenty-four hours in water, which *dissolves out* the chromate of mercury for the most part, leaving however a yellow tint on the ground, which resists obstinately. But though pretty effectually fixed in this way against *light*, they are not so against *time*, as they fade considerably on keeping.

229. When the proto-nitrate of mercury is mixed, in solution, with either of the ammoniacal double salts, it forms a precipitate, which, worked up with a brush to the

consistency of cream, is easily (and with certain precautions of manipulation\*) very evenly spread on paper, producing photographic tablets of every variety of sensibility and inertness, according to the proportion of the doses used. By combining all three of the ingredients, and adding a small quantity of tartaric acid†, a paper is produced of a pretty high degree of sensibility (more than by the use of either separately), which in about half an hour or an hour, according to the sun, affords pictures of such force and depth of colour, such velvety richness of material, and such perfection of detail and preservation of the relative intensities of the light, as infinitely to surpass any photographic production I have yet seen, and which indeed it seems impossible to go beyond. Most unfortunately, they cannot be preserved. Every attempt to fix them has resulted in the destruction of their beauty and force; and even when kept from light, they fade with more or less rapidity, some disappearing almost entirely in three or four days, while others have resisted tolerably well for a fortnight, or even a month. It is to an over-dose of tartaric acid that their more rapid deterioration seems to be due, and of course it is important to keep down the proportion of this ingredient as low as possible. But without it I have never succeeded in producing that peculiar velvety aspect on which the charm of these pictures chiefly depends, nor anything like the same intensity of colour without over-sunning.

230. I might here describe many other curious and interesting photographic results to which, under the genial influence of such a summer as, possibly, has never before been witnessed in England, I have been conducted. But in so doing I should surpass the reasonable bounds of a Postscript illustrative of my text, and abuse the privilege accorded me. Yet I cannot forbear noticing one at least, in which a line or dot engraving of any degree of delicacy is imitated, line for line, and dot for dot in a manner which might deceive any but a practised artist to the point of rendering him unable to declare that the photograph had *not* been struck off from the original plate with common printing ink, by the ordinary process of copper-plate printing. The details of this process, which are delicate and somewhat tedious, cannot properly be stated here; if for no other reason, because I have not yet obtained a complete command over the result: but a microscopic examination of the specimens placed in the hands of our worthy Secretary, though somewhat marred by the accidents of manipulation, will I think suffice to justify the terms employed above.

\* The cream should be spread as rapidly as possible over the whole paper, well worked in, cleared off as much as possible, and finished with a brush nearly dry, spread out broad and pressed to a strait thin edge, which must be drawn as lightly and evenly as possible over every part of the paper till the surface appears free from every streak, and barely moist.

† One measure of a solution of ammonio-citrate, and one of a solution of ammonio-tartrate of iron, containing, each, one-tenth of its weight of the respective salts. Tartaric acid, saturated solution, one-eighth of the *joint volumes* of the other solutions. Form a cream by pouring in as rapidly as possible one measure of a saturated solution of the proto-nitrate and well mixing with a brush.

